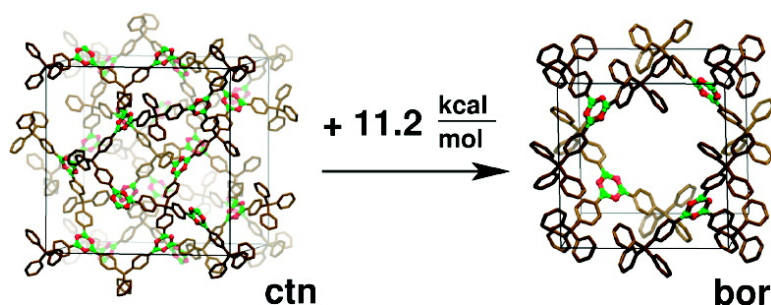


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An Accurate Force Field Model for the Strain Energy Analysis of the Covalent Organic Framework COF-102

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By introducing the concept of reticular synthesis, Yaghi et al. propelled the field of coordination polymers in an exciting new direction.^{1,2} Especially the research on carboxylate based Metal Organic Frameworks (MOFs) is rapidly increasing, due to their potential in gas storage (in particular for hydrogen) and separation, as well as in catalysis.³ An alternative series of frameworks, based only on organic building units connected by covalent bonds (Covalent Organic Frameworks; COFs), has been introduced recently.⁴ Using trigonal and tetrahedral vertices a porous (3,4)-connected three-dimensional network is formed.

By the slow self-condensation of tetra(4-dihydroxyborylphenyl) methane **1** (Figure 1) the material COF-102 can be synthesized under formation of trigonal boroxin B_3O_3 rings.⁴ Interestingly, the structure of this polycrystalline material could be resolved using the assumption proposed by O’Keeffe and Yaghi et al., namely that one of the two most symmetric (edge transitive) nets with trigonal and tetrahedral vertices will be formed.⁵ These nets with the acronyms **ctn** and **bor** (derived from carbon nitride and boracite) are shown in Figure 2 in their augmented form.⁶ The **ctn** structure could unambiguously be assigned to COF-102 based on a comparison of simulated and measured powder X-ray diffraction patterns. It was already speculated that a lower strain in the **ctn** net could be a possible reason for this preference.⁴

In this contribution we present an accurate molecular mechanics (MM) force field, parametrized explicitly for COF-102 on the basis of first principles calculations of nonperiodic model systems, and apply it to analyze the relative strain energy for these structures. It is very important to realize that these 3D-networks can be considered as supramolecular conformers. They contain the same number of atoms and share the same connectivity. Thus, both nets belong to the same MM potential energy surface, and it is possible to compute relative energies. However, unlike the boat and chair conformation of cyclohexane, the nets can not interconvert without breaking bonds.

To our knowledge, all MM investigations of COFs focused on guest molecule adsorption and diffusion, using generic force fields and frameworks constrained to the experimental structure,⁷ and our force field represents the first fully flexible model for COFs. The general recipe for the parametrization followed our recent work on zinc carboxylate based IRMOFs.⁸ In this case we have employed our newly developed Genetic Algorithm (GA) based parametrization approach, which will be described elsewhere.⁹ For technical details see also the Supporting Information (SI). We used the two nonperiodic models tetraphenylmethane **2** and triphenylboroxin **3** (Figure 1) to extend the parametrization of the MM3 force field.¹⁰ Force field parameters were fitted by the GA approach to reproduce both structure and normal modes of the models calculated by (hybrid) density functional theory (DFT; B3LYP/cc-pVDZ level; see SI for further details).

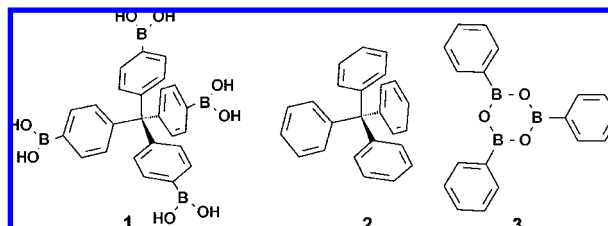


Figure 1. Monomer (**1**) and nonperiodic model systems (**2**, **3**) of COF-102.

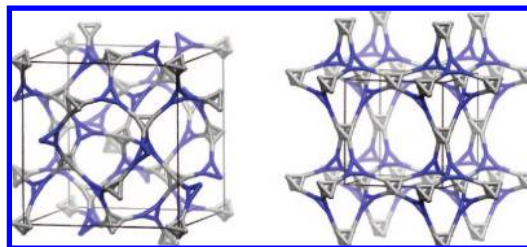


Figure 2. Augmented networks **ctn** and **bor**.

Due to the different chemical environment we discarded the available parameters for boronic acids¹¹ and readjusted all terms in **3** involving a boron atom. Especially for the low frequency modes, relevant for structural deformations to reduce strain, an excellent fit was achieved by the GA approach. For example the normal-mode frequency for the symmetric buckling of **3**, which is strongly deformed in the **bor** structure (see Figure 3b), is calculated to be 35.2 and 37.2 cm^{-1} at the DFT and the MM3 level, respectively. For the hydrocarbon **2** the MM3 standard parameter set is in principle complete. However, it erroneously gives a D_{2d} symmetric minimum energy structure for **2**, whereas experimental data as well as previous theoretical studies indicate a structure with a lower S_4 symmetry.¹² On the DFT level we found a preference of 0.71 $kcal\ mol^{-1}$ for the S_4 structure. Because of the well-known underestimation of dispersive interactions in DFT we confirmed this by a single-point MP2 calculation, which gave an even higher relative stabilization of 1.7 $kcal\ mol^{-1}$ for the S_4 structure with respect to the D_{2d} transition state. Thus, we readjusted the relevant C2–C2–C1–C2 torsion term for the central sp^3 carbon in **2** (where C1 and C2 represent an sp^3 and sp^2 carbon atom, respectively, following the MM3 nomenclature). With this reparametrization the DFT structures and normal modes for both the S_4 minimum and the D_{2d} transition state were accurately reproduced by the force field, with an energy barrier of 1.5 $kcal\ mol^{-1}$ (see Table 1).

The structures of COF-102 in the **ctn** and **bor** network were generated by replacing the network vertices (taken from the RCSR database)⁶ with the properly positioned building blocks CPh₄ (Ph = C₆H₄) and B₃O₃. The systems were minimized in energy using

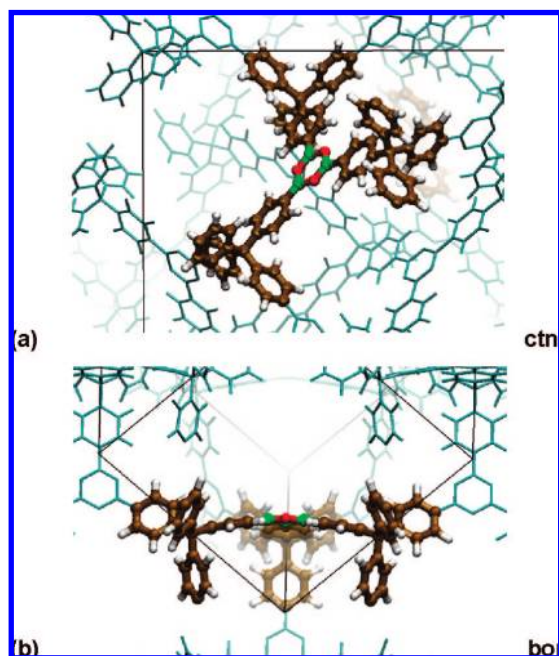


Figure 3. Trigonal vertex environment in the **ctn** (a) and **bor** (b) net.

Table 1. Comparison of Geometric, Vibrational, and Energetic Data of Model System **2** and COF-102 (Angles, deg; Vibrational Modes, cm^{-1} ; Energies, kcal mol^{-1})

	2 (DFT)		2 (MM3)		COF-102 (MM3)	
	S_4	D_{2d}	S_4	D_{2d}	ctn	bor
α (C2–C1–C2) ^a	105.8	102.3	105.5	102.0	106.1	101.2
β (C2–C1–C2') ^a	111.4	113.2	111.5	113.4	111.2	113.8
τ (C2–C2–C1–C2) ^a	126.2	86.1	126.8	88.1	129.5	87.1
ν^b	23.8	i19.0	29.8	i23.4	-	-
ΔE	0.0	0.71	0.0	1.51	0.0	11.2 ^c

^a C2: sp^2 carbon atom; C1: sp^3 carbon atom; a prime marks a second atom, not symmetry related by the C_2 main axis; for a detailed definition of the structural parameters of **2**, see SI. ^b Lowest or imaginary vibrational mode. ^c Per formula unit $[\text{CPh}_4]_3[\text{B}_3\text{O}_3]_4$.

our extended MM3 force field in a periodic cell in space group $P1$ with respect to all degrees of freedom and the cell parameters. The resulting cell size of 27.03 Å for the **ctn** net compares very well with the value of 27.177(1) Å derived from experiment (LeBail extraction).⁴ Note that the unit cell of **bor** contains one formula unit $[\text{CPh}_4]_3[\text{B}_3\text{O}_3]_4$, whereas **ctn** contains four, and relative energies are thus given per formula unit. In accord with the experimental observations we find the **ctn** network is more stable by 11.2 kcal mol^{-1} (Table 1). In Figure 3 closeup views of the boroxin ring with the three adjacent CPh_4 units are shown for both structures. For **ctn** the triphenylboroxin unit is basically planar, whereas in the case of **bor** it is substantially buckled. This is due to the large deviation from tetrahedral symmetry for the four coordinated vertex in **bor** (see also Figure 2). To reduce the strain in the CPh_4 units, the small angle α of 70.5° in the idealized network is widened to 101.2°, and the B_3O_3 unit is moved away from the ideal trigonal vertex position. The energetic penalty for this deformation, corresponding to the above-mentioned buckling mode of **3**, is well represented in our force field due to accuracy with which the DFT calculated vibrational frequency is reproduced. The second reason

for the preference of **ctn** is also visible in Figure 3: the conjugation of the C–B bond enforces the C_6 and the B_3O_3 rings to be coplanar. In the case of **ctn** this leads to an S_4 symmetric conformation of the CPh_4 moiety, similar to the gas phase structure of **2**. The same conjugation locks the CPh_4 unit into the transition state structure of higher D_{2d} symmetry in **bor**. This is also seen by comparing the valence angles α and β and the torsion angle τ of the two periodic systems and the model system **2** given in Table 1. Thus, there are two steric strain effects in **bor** with a similar magnitude,¹³ leading to a thermodynamic preference for the **ctn** net. It is important to note that with the original MM3 parametrization, which prefers the D_{2d} structure of **2**, the **bor** net is erroneously calculated to be of slightly lower energy than **ctn**.

We have for the first time shown that, by parametrization of a force field on the basis of theoretical first principles data, the relative strain energy and thus the thermodynamic preference for a network structure of a porous organic linker based framework (like a COF or MOF) can be determined without any experimental input. For COF-102 the **ctn** structure is predicted to be preferred in accord with experiment, which proves that here, indeed, a reduction of steric strain and no kinetic or solvent templating effect is governing. Our findings also demonstrate that a very accurate parametrization is needed, since even small errors can add up for the periodic structure. Because of the atomistic model it is additionally possible to analyze the origin of the strain effects in detail. However, in case of a small difference in the strain energy, solvent templating, entropic, or kinetic effects will play the major role in determining the network topology, which are not covered by our current model. We are currently expanding our approach to other COF and MOF frameworks.

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Supporting Information Available: Details about the parametrization procedure, force field parameters, and Cartesian coordinates and energies of the calculated systems. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) Assuming an energy penalty of 1.5 kcal mol^{-1} for each of the three D_{2d} symmetric CPh_4 units in the **bor** structure, a strain of ~ 6.5 kcal mol^{-1} results for the buckling of the boroxin unit.

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